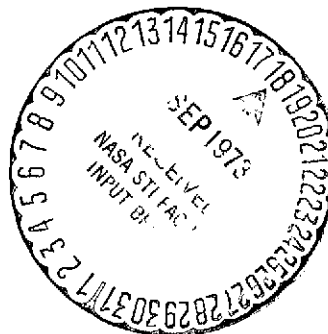


SIMULATION OF THE ROLE OF MICRO-ORGANISMS
DURING ORE FORMATION IN LAKES

D. R. Gabe

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SIMULATION OF THE ROLE OF MICRO-ORGANISMS
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D. R. Gabe \

There are differences of opinion in an evaluation of the role of microorganisms in the formation of iron-manganese ores in lakes (as well as in the sea). Contrary to the views of microbiologists (Perfilyev, 1926, 1952; Perfilyev, Gabe, 1961, 1964; Sokolova-Dubinina, Deryugina, 1967a, b, 1968; Kuznetsov, 1970, and others), the majority of geologists usually do not even consider the bacterial factor in the formation of ore concentrations even at the stage of an early diagenesis, when treating the mechanism of the depository ore-forming process. The abiogenic concept is expressed most consistently in the works of N. M. Strakhov, who rejects in principle any possibility of a significant and specific role of microorganisms in the iron- and manganese-ore process (Strakhov, 1947, 1965; Strakhov et al., 1968).

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By growing organisms on laboratory cultures, it became possible in a number of cases to discover specific microbes at the sites of formation of iron-manganese ores, to separate some of these organisms into elective symbiotic silts or, sometimes, into pure cultures, and

* Numbers in the margin indicate pagination in the original foreign text.

to demonstrate their ability to oxidize iron and manganese. Our views on the fine microscopic structure of these microorganisms have been repeatedly confirmed. Application of the electron microscope in recent years (Zavarzin, 1963; Balashova, 1967, 1969; Duvina, 1969, 1970) enabled us to reveal also the submicroscopic features of their organization. However, the method of laboratory growth on synthetic cultures is not really sufficient for discovering new microorganisms participating in the formation of ores in lakes, for study of rather specific ecology and complex natural life cycles of the manganese- and iron-oxidizing microbes, and the extent of their geochemical activity. It is difficult to establish by this laboratory method the actual participation of given organisms in the role of biocatalysts for concentration of the Mn and Fe oxides in the bottom deposits, and it is difficult to prove finally that this geochemical process cannot take place in nature in the absence of specific microbes, including the known ones. The experimental chain of evidence usually contains the third and decisive postulate of the triade of Koch: the isolated manganese- and iron-oxidizing organisms do not succeed in reproducing the process of concentration of both the elements under conditions and in forms similar to those in nature. This situation is the reason for controversy between the microbiologists and the geologists.

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The fulfillment of the third link of the triade is complicated, moreover, by the fact that the deposited iron-manganese ores, just like many other natural formations and processes, are not the products of the vital activity of single pure bacterial cultures. Rather, they are the result of the prolonged existence of specific microbiocenoses firmly established during a very long period, as noted already by S. N. Vinogradskiy (1952) in the case of the soil microflora. Moreover, the microbiology of biocenoses, so important for understanding the geological activity of microbes, is still not methodically developed to a sufficient degree, and is limited so far to a microscopic, mostly descriptive in character, investigation of microbial landscapes.

In order to clarify the actual role of specific microorganisms in the formation of iron-manganese ore nodules in the silt, i.e., in order to fulfill in the usual sense the third link of the triade of Koch, we can continue the simulation of this process on corresponding laboratory models. In contrast to a number of other geochemical phenomena, the process of formation of iron-manganese layers in lake deposits — which occurs with the aid of specific microflora, as was found by us earlier (Perfilyev, Gabe, 1964) — is fully satisfactory for modeling on the basis of microzonal theory of silt formation postulated by V. V. Perfil'yev (1929, 1932, 1952). Of particular significance are the widely dispersed microzones of conversion (which he discovered in the silt, i.e., concentration of a number of geochemical processes in thin layers, because of a fine laminar distribution and multiplication of many microorganisms in the silt layers. The conversion microzones, dependent on the activity of the silt microflora, are reestablished in the silt relatively fast if they are disturbed. They may form again in a small amount of pre-mixed silt material, giving rise to a secondary diagenetic silt profile.

Core samples taken from many lakes in the humid zone, particularly from oligotrophic lakes, exhibit frequently sharply defined microzones (layers) near the surface, consisting of manganese oxides or hydrate of iron oxide. Their universal distribution has been noted also in the geological literature. However, the laboratory media would not easily show that these iron-manganese intercalations are not of a purely chemogenic nature, but are the product of the vital activity of microorganisms stratified finely in the silt. If, however, these layers are regarded as the conversion microzones, then we can reproduce them in core samples withdrawn from a suitable water reservoir and placed into a vessel. This is because our numerous observations have indicated that even a limited volume of silt contains all the material necessary for biogenic conversions of manganese and iron in a long period of time.

Therefore, for a simple and easily-realized model, we adopted the laboratory simulation method in small vessels of the secondary diagenetic silt profiles with conversion microzones. In their

original elementary form, they represent the basic mechanism of the concentration of iron- and manganese-oxides in the silts (Perfil'yev, Gabe, 1964).

The present paper reports some new results of using this method in studies of microbiology of the initial stage of the iron-manganese ore deposition. These studies were conducted on two lakes of Karelia Isthmus: Punnus-yarvi (Red Lake) and Kirkko-yarvi (Pravdinskoye Lake).

It is necessary to point out that the Punnus lake has been the object of many investigations with regard to its ore formation. These investigations were many-sided: limnological (Semenovich, 1958), physico-chemical (Sokolova, 1962), geochemical (Strakhov et al., 1968), and microbiological (Sokolova-Dubinina, Deryugina, 1967a, b). This circumstance proved to be very significant in establishing the similarity of our model to the natural processes of ore formation in the lake, since these authors carried out their investigations in the water basin itself, i.e., directly in the primary silt profile.

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The basic aim of experiments with the secondary silt profiles, described in this paper, was to clarify the reasons for, and the conditions of, the sharp variations in the quantitative ratio of the oxides of Mn and Fe in depository ore formation in lakes. The same question presented itself to other authors studying the iron-manganese ores in lakes and soils (Naumann, 1922; Krauskopf, 1963; Make-donov, 1966; and others). However, according to our view, this problem has never received a sufficiently accurate solution, because of underestimation of the geochemical activity of microorganisms.

As a starting point for our investigations, we used the results obtained in previous studies (Perfil'yev, Gabe, 1964). We found then that Metallogenium, and sometimes Caulococcus and others, serve as concentrators of manganese in silt layers in the form of its oxides, and that the Siderococcus or analogous iron bacteria widely distributed in lakes function as the main concentrators of the iron

oxide. However, sedimentations of the manganese microbe Metallogenium contain usually a small admixture of iron oxide. This admixture reaches sometimes 30%, but usually amounts to only 3 - 5%.

In order to establish the dependence between the ratio of the Mn and Fe oxides in the layers of oxidizing microbes and the content of lower-oxidation-state ions of these elements in the silt solution, we carried out 12 experiments in the period from 1963 to 1968. These experiments involved more than 120 vessels with secondary profiles from bottom deposits of the lakes of Punnus-yarvi (seven series of containers) and Kirkko-yarvi (five series).

The deposits collected in 1963, 1965, and 1967 served as the initial material. Samples obtained from the region of the large ore field of Punnus-yarvi (Station 5) were utilized further in the series of containers XIII, XV, XXI, XXII and XXVIII. Samples from Punnus-yarvi near the shore in shallow waters where large ore concretions were seldom encountered (Station 6) were utilized in the series of vessels XVI and XIX. The samples from Kirkko-yarvi in the region of the ore field near Punnus-ioki were subsequently employed in the series XVII, XVIII, XXIII, XXIV, and XXVII. Each of the series of vessels represented a separate experiment.

Experimental tests performed on containers of these series included the determination of pH and Eh of the reducing layer and Eh of the oxidation microzone; the content of Mn^{2+} and Fe^{2+} ions in the silt solution, and sometimes in water adjacent to the bottom; and the analysis of the content of sediments formed by oxidizing microorganisms, to clarify the relation of the oxides of manganese and iron with the preliminary microscopic inspection of these microgrowths at various stages of the formation of the microzonal secondary profile. The experiments with various series lasted from 2 to 4 years, with periodic repetition of analyses. This procedure permitted us to follow the dynamics of formation of secondary profiles, and to establish changes in microbial landscapes and in iron-manganese biogenic deposits.

The first experiments with silts (series XIII, XV, XVI, XVII) revealed large differences in the secondary silt profile depending on the water basin and the station. For the development of a manganese microzone in the silt profile formed by the typical Metallogenium — in addition to the presence of Mn^{2+} ions in the silt solution, which are usually there in sufficient quantity — it is necessary to have an appropriate redox potential of the silt sample. The Eh of the reducing layer should be higher than that required for the formation of the iron oxidation microzone. It is for this reason /576 that the manganese microzone (Metallogenium) is absent in vessels of the series XVI, containing silt characterized by a very low Eh, despite the abundance of divalent manganese in the silt solution. Under such conditions, the divalent manganese is not retained in the silt, but diffuses into the bottom-adjacent water, where it can be discovered easily (Table 1).

One could conclude from these observations that it is necessary to increase the redox potential (Eh) of the silt, to facilitate the formation of a manganese microzone in the secondary diagenetic profile. Such an increase is easily achieved by the addition into the silt sample of a powdered iron-manganese lake ore, which has an increased Eh, particularly when it contains a considerable amount of manganese dioxide.

Table 2 gives brief results of an experiment (Series XIX) in which a ground ore from the lake Punnus-yarvi was added to the silt sample withdrawn from Station 6 of Punnus-yarvi. This location is characterized by a low Eh, and by the absence of a manganese microzone and Metallogenium (Table 1, Series XVI).

In this experiment, an increase of the redox potential, caused by the addition of powdered lake ore (both sterilized and "alive"), led to the suppression of the microzonal oxidation of iron as a result of nearly complete disappearance of divalent ions from the silt solution. The secondary profile contained only a black-brown layer of manganese, and the peloscopes contained a black-brown precipitate,

TABLE 1. DEPENDENCE OF THE OXIDATION MICROZONE ON THE REDOX POTENTIAL OF THE SILT SAMPLE (1963)

Series (Ex- peri- ment)	Lake station, month of tak- ing the pack- ing	Initial silt sample	Secondary silt profile			
			Eh, volts, oxd/red	Content in silt solution, redn layer		Character of oxidn. microzone; microflora oxidn. layer in pelo- scope
				Mn ²⁺ , mg/l	Fe ²⁺ , mg/l	
XIII	Punnus-yarvi, Station 5, June-July	Dark-cinnamon, very many iron-manganese concretions	0.79-0.83 0.25-0.35	15-20	0	A black-brown thin Mn layer only; typical Metallogenium only
XV	Punnus-yarvi, Station 5, July-August	Cinnamon, many iron-mangan- ese concre- tions	0.78-0.80 -0.10-0.15	20-30	0	An abundant black-brown Mn layer from typical Metallogenium, followed by a delayed poorly- defined microzone with sparse Siderococcus
XVI	Punnus-yarvi, Station 6, July-August	Olive-grey, almost with- out con- cretions	0.55-0.57 -0.25-0.30	50-120	10-15	A yellow-cinnamon Fe microzone, primarily from Siderococcus. Absence of Metallo- genium

(Table continued on following page)

TABLE 1. (Continued)

Series (Ex- peri- ment)	Lake station, month of tak- ing the pack- ing	Initial silt sample	Secondary silt profile			
			Eh, volts, oxd/red	Content in silt solution, redn layer		Character of oxidn. microzone; microflora oxidn. layer in pelo- scope
				Mn ²⁺ , mg/l	Fe ²⁺ , mg/l	
XVII	Kirkko-yarvi, July-August	Cinnamon, many iron-mangan- ese concre- tions	0.70-0.75 -0.25	15-40	5-10	A two-layer oxidation microzone. Ocher-colored deposit of <i>Siderococcus</i> , and a brown deposit of typical forms of Metal- logenium

Note. The concretions in samples were filtered off, before packing the silt into vessels.
Oxidn layer — oxidation layer; redn layer — reduction layer.

TABLE 2. TRANSITION FROM MICROZONAL OXIDATION OF IRON TO OXIDATION OF MANGANESE AS A RESULT OF ADDING LAKE ORE TO THE SILT SAMPLE

No. of vessel with silt	Change in composition of silt	Color of silt in secondary profile	Eh, volts, oxidn layer redn layer	Content in silt solution redn layer		Microflora of oxidn layer (in peloscopes)
				Mn ²⁺ mg/l	Fe ²⁺ mg/l	
Control P 3128 P 3129	Initial silt (sample from Punnus-yarvi Stn. 6)	Olive-grey with ocher-colored and light-brown microzones	0.63-0.67 -0.25	30-55	11-13	Much of Siderococcus as abundant ocher-colored deposit. Absence of typical Metallogenium in brown deposit
Experiment Vari- ant 1 P 3130 P 3131	Silt + dry sterile lake ground ore	Grey-cinnamon silt with black-cinnamon oxidn microzone	0.72-0.75 0.18-0.23	20-30	0	Abundant manganese deposit, but black small drop-like forms instead of typical Metallogenium
Experiment Vari- ant 2 P 3134 P 3135	2/3 of silt + 1/3 of dry powdered ore	Ditto	0.73-0.76 0.18-0.25	25-40	0-2	Quite abundant black-cinnamon deposit, but some zoogeleic mineralized agglomerates instead of typical Metallogenium

but this silt sample contained no components which are required for normal development of Metallogenium. The latter was observed in a nontypical form, i.e., without signs of radial-lobe structure of cenobia. A similar disturbance of the development cycle of Metallogenium was observed in silt samples which were subjected to thermal treatment in order to destroy the silt fauna, which greatly disturbed the microzonal structure of the secondary profile. After heating for 30 minutes at 60 - 65°, the fauna in the silt disappeared and an apparently normal secondary silt profile with a characteristic black-brown microzone began to develop in containers. A deposit was formed in the peloscopes, but it had rather diffuse features, and consisted only of nontypical zoogeleic agglomerates of Metallogenium.

The experiment also used silt samples from Lake Kirkko-yarvi, characterized by a lowered value of Eh (Series XVII in Table 1). In the formation of the secondary microzonal profile, these silts always developed a typical two-laminar layer — from a black-brown manganese microzone and, underlying it, an ocher-colored iron microzone. The manganese microzone consisted of the growths of Metallogenium (in typical and nontypical form), and the iron microzone was composed of the agglomerates of Siderococcus. A ground iron-manganese ore was also added to the samples in order to increase the redox potential to such a degree as to prevent the reduction of iron in the silt and to secure the development of only the manganese-oxidizing microorganisms. Experiments with the secondary silt profiles from Kirkko-yarvi were set in vessels of the Series XVIII (in 1963), and later in Series XXIII (1965).

The results, which proved to be similar in both the experiments, are presented graphically in Figure 1 for the series XVIII, and in Figure 2 for the Series XXIII. These graphs show changes which occurred during two years in the control vessels (A) and experimental vessels (B) of both series. The values shown are the Eh in a reducing layer and in an oxidation microzone of manganese, the amount of Mn^{2+} and Fe^{2+} ions in the reducing layer of the silt solution, and the value of pH. The plots give average values for the control and experimental vessels.

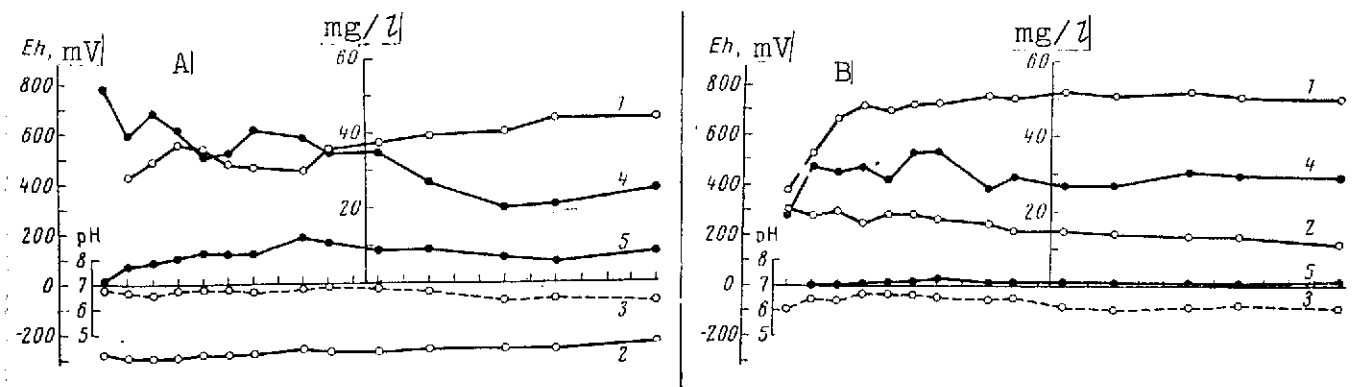


Figure 1. Formation of the secondary microzonal profile in silt from Kirkko-yarvi (Series XVIII): A — in control vessels with original silt; B — in experimental vessels with added ore. The horizontal coordinate shows the time in months, and the vertical coordinate gives Eh in mV, the pH and concentration (mg/l); 1, 2 — the Eh curves of the oxidation microzone of Mn and Fe (1) and of the reducing layer (2); 3 — the pH curve; 4, 5 — concentration curves of Mn^{2+} (4) and Fe^{2+} (5) of the reducing layer of silt solution

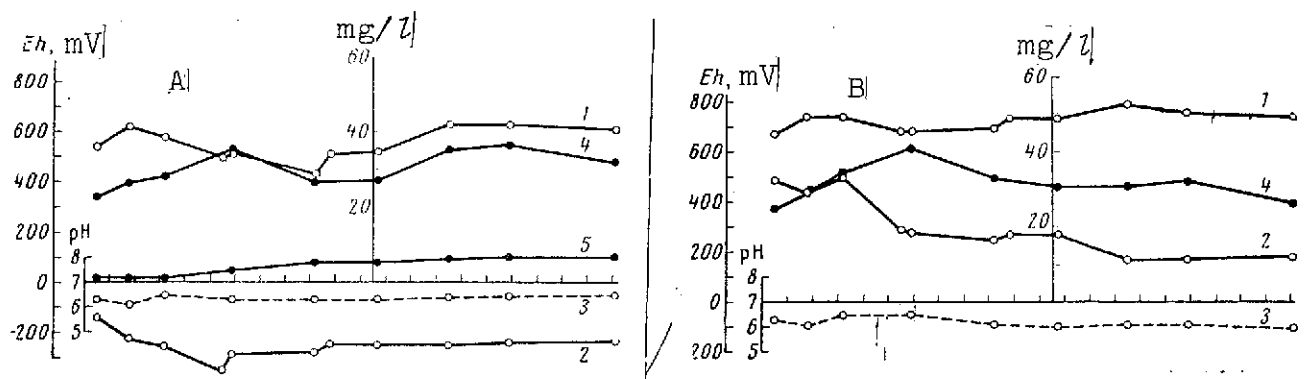


Figure 2. Formation of the secondary microzonal profile in silt from Kirkko-yarvi (Series XXIII): A — in control vessels with original silt; B — in experimental vessels with added ore. Notation is the same as in Figure 1

The addition of powdered iron-manganese ore to the sample resulted in a sharp increase of Eh of the reducing layer of the silt profile, from -0.28 to 0.25 - 0.29 volts. Concentration of Mn^{2+} in silt solution showed practically no change, but the amount of Fe^{2+} ions dropped sharply: from 8 - 10 mg/l (control) to 1 - 2 mg/l in

Series XVIII, and from 5 - 6.5 in the control to zero in experimental vessels in Series XXIII. The oxidation microzone had a lower potential in the control vessels (i.e., without the addition of ore); its Eh was 0.5 - 0.7 volts in Series XVIII and 0.5 - 0.6 volts in Series XXIII. The Eh of the oxidation microzone in experimental vessels (i.e., after addition of ore) reached 0.75 - 0.8 volts and 0.7 - 0.78 volts, respectively. This increase resulted, apparently, from the enrichment of the oxidation microzone in experimental vessels with manganese oxides. The intensive black-brown sediment in peloscopes consisted of copious aggregates of Metallogenium in its typical radial form, primarily of strongly mineralized cenobia.

Analogous experiments were performed with silts of two samples taken in 1963 and 1965 in the area of the large ore deposits of Lake Punus. The following changes of the redox potential, caused by the addition of powdered lake ore to the original silt samples, were observed in the reducing layer of secondary silt profiles developed in vessels of two series (XXI and XXII):

Series	Year of sample	Eh (volts) of control vessel	Eh (volts) of experimental vessels
XXII	1963	0.11 - 0.14	0.30 - 0.35
XXI	1965	-0.10 - -0.13	0.10 - 0.12

The control vessels of Series XXI with the lowest Eh of reducing layer exhibited a sharply-defined double-layer stratum of black-brown microzone of manganese oxide and yellow-orange microzone of iron oxide. One could see in the peloscopes double-layer deposits: a black one — copious agglomerates of Metallogenium, mainly in the form of trichospherical and radial-lobe cenobia, and underlying them ocher-colored microgrowths of Siderococcus.

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The secondary silt profiles in experimental vessels of Series XXI and in control vessels of Series XXII were similar. This similarity should be expected because of the closeness of values of the

redox potential of the reducing layer. The former exhibited some weakly-developed iron laminae, whereas the latter showed no such layers. But both groups of the vessels showed a clearly delineated black-cinnamon microzone of manganese oxide in the silt. There was none, or only sparsely developed, *Siderococcus* in the peloscopes, and the deposits consisted of abundant typical Metallogenium with radial cenobia, somewhat more mineralized than in the control vessels. of Series XXI. The oxidation microzone of the reducing layer in experimental vessels of Series XXII, which had the highest redox potential, was of black color, and black deposits in the peloscopes consisted of typical Metallogenium with the predominance of strongly mineralized radial-lobe and spherical-nodular cenobia. The direct reason for suppression of iron-oxidizing activity of microorganisms in the silt profile of experimental vessels of Series XXI and all the vessels of Series XXII was the absence of Fe^{2+} ions in the silt solution or a sharp decrease in their amount as a result of an increase of Eh of the reducing layer.

Manganese and iron of the lake ore and minerals become reduced and pass into solution only with the assistance of microorganisms of such, for instance, heterotrophic bacteria as *Bacillus circulans*, *B. mesentericus*, *B. cereus*, *B. polymyxa*, and others. All these bacteria are facultative anaerobes, and the reduction of iron and manganese is not absolutely necessary necessary for their vital activity. Normally they multiply in substrates containing no oxides of iron and manganese, and with the free access of the oxygen of air (Sokolova-Dubinina, Deryugina, 1967a, b; Troshanov, 1964, 1968, 1969). Hence, one could expect that suppression of the bacteriogenic process of reduction of iron hydroxide in silt, occurring as a result of an increase of its redox potential (after addition of such a naturally oxidized product as iron-manganese ore), should not result in a loss of the reducing capacity of these microorganisms.

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To clarify this point, substrate "A" of Bromfield with the lake ore was seeded from the control and experimental vessels, i.e., those having an increased redox potential and [lacking] the reduced iron in silt solution. The investigation was carried out on silts

from Lake Punnus (Series XXI) and from Lake Kirkko (Series XXIII, XXIV and XXVII) soon after formation of the secondary silt profiles. For some of the vessels, such a seeding was repeated after three years (Series XXI). The results are presented in Table 3. The control and experimental vessels differed greatly with respect to the

TABLE 3. RETENTION OF REDUCING CAPABILITY OF SILT MICROFLORA AFTER STAYING IN SILT HAVING A HIGH REDOX POTENTIAL — 1965 (Eh IN VOLTS, Mn^{2+} and Fe^{2+} in mg/l)*

Lake, Series, date of laying	Date of seeding	Seeding from control vessels				Seeding from experimental vessels			
		Ves- sel No.	In culture			Ves- sel No.	In culture		
			Mn ²⁺	Fe ²⁺	Eh		Mn ²⁺	Fe ²⁺	Eh
Punnus-yarvi XXI Nov. 15	19 II. 1966	5151	86,7	22,5	-0,25	5154	31,0	17,5	-0,26
		5152	98,0	30,0	-0,26	5155	67,0	21,6	-0,27
	7. VI. 1. 1969	5151	204	19,5	—	5154	182	20,2	—
		5152	181	13,2	—	5155	228	31,6	—
Kirkko-yarvi XXIII Nov. 17	18 II. 1966	5178	65	14,7	-0,11	5184	78,7	25,3	-0,12
		5179	105	26,9	0,02	5186	58,3	16,6	-0,15
Kirkko-yarvi XXIV Nov. 20	19. II. 1966	5197	73,3	31,0	-0,24	5201	58,4	18,2	-0,25
		5198	98,8	65,0	-0,05	5202	81,8	22,5	-0,23
Kirkko-yarvi XXVII March 31	7. VIII. 1969	8227	190	12,2	—	8231	221	22,2	—

* Commas represent decimal points.

Eh of the reducing layer, particularly in Series XXIII, XXIV and XXVII, where the difference reaches 0.6 - 0.7 volts. The seedings of experimental vessels of all series show approximately the same amount of Fe^{2+} as the seedings of control vessels. The same applies to lowering the Eh of the substrate. Consequently, the reducing microbes can exist without harm in silt with a high redox potential, and only when this potential is lowered to the level which permits retention in the solution of the ferrous form of iron do these

microbes begin to function as iron-reducing organisms. The limiting factor for the formation in silt of ferrous iron is the increased level of the redox potential, and not the lack of iron-reducing microbes which are present everywhere, or the lack of ferric iron — which is plentiful in lake silts, particularly in deposits of ore-containing lakes.

The content of divalent ions of iron and manganese in a silt solution governs the ratio of the oxides of these elements in ore layers (microzones) formed in the silt. This statement is confirmed by a comparison of the analyses of microgrowths in peloscopes for their content of the Mn and Fe oxides, and the determination of Mn^{2+} and Fe^{2+} concentrations in the silt solution of the reducing layer of the same vessels. The main results of chemical analyses of the nine series of vessels with secondary silt profiles from Lakes Punnus and Kirkko are presented in Table 4. The amount of oxides of manganese and iron, found in peloscopes and comprising the main mass of sediments, was calculated from the formulas Mn_2O_3 and Fe_2O_3 and was shown in percent of the sum of both oxides. The Eh was obtained from readings of stationary platinum electrodes, and was included in the Table in the form of the average number of determinations in the course of the experiment. The concentrations of Mn^{2+} and Fe^{2+} ions, determined periodically in the silt solution withdrawn from collodion cells, are also presented in the Table in the form of average values. The data for the first five series indicate the reproducibility of results in parallel vessels. Therefore, in order to shorten the Table, the data for parallel vessels in the next four series (XXI, XXIII, XXVII and XXVIII) are combined and averaged.

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A lowering of the concentration of the Fe^{2+} ion and its nearly complete extinction (to an amount not determinable in the analysis of 1 - 1.5 ml of silt solution), caused by an increase of Eh of the silt solution, leads to a reduction of the percent of Fe oxide in microgrowths (Table 4). This occurs because of the extinction of

TABLE 4. RELATION BETWEEN THE CONTENTS OF Mn^{2+} AND Fe^{2+} IN A SILT SOLUTION OF THE REDUCING LAYER AND THE RATIO OF THESE ELEMENTS IN ORE LAYERS FORMED BY MICROBES*

Lake, Series	Composition of silt (s), addition of ore (o)	Vessel No.	Silt solution			Microgrowths in peloscopes		
			Avg. Eh, V	Avg. Mn^{2+} mg/l	Avg. Fe^{2+} mg/l	Mn_2O_3 %	Fe_2O_3 %	Composition of microflora
Punnus XIII	Initial silt	{31	0,35	21	0	97,8	2,2	Black deposit of typical Metallogenium, primarily radial-vane cenobia
		{32	0,32	19	0	97,1	2,9	
		{33	0,29	20	0	96,8	3,2	
		{38	0,13	18	0	97,8	2,2	
Punnus XV	Ditto	{392	0,0	27	0,1	90,0	10,0	Black deposit of typical Metallogenium in radial-vane form. An ocher-colored deposit of Siderococcus appeared later
		{393	-0,10	21	0,3	93,7	6,3	
		{394	-0,09	18	0,5	95,0	5,0	
		{396	-0,15	22	0,3	96,2	3,8	
Kirkko XVII	Ditto	{3108	-0,26	19	5,0	73,4	26,6	Nontypical Metallogenium. Copious Siderococcus
		{3111	-0,28	24	6,4	65,2	34,8	
		{3112	-0,26	19	6,5	79,6	20,4	
Kirkko XVIII	Control (initial silt)	{3117	-0,26	27	6,6	74,7	25,3	Nontypical Metallogenium. Copious Siderococcus.
		{3118	-0,25	36	8,0	70,0	30,0	
	Experimental (3/4 s + 1/4 o)	{3120	0,11	23	1,3	90,1	9,9	Only Metallogenium in typical radial form
		{3121	0,11	31	0,7	95,0	5,0	
Punnus XIX	Experimental (1/2 s + 1/2 o)	{3123	0,24	29	0,7	82,6	17,4	Only typical Metallogenium, mostly zooglycic and spherical-nodular forms
		{3124	0,24	27	0,6	88,4	11,6	
	Control	{3128	-0,24	32	9	69,4	30,6	Nontypical Metallogenium, copious Siderococcus
		{3129	-0,24	41	11	64,2	35,8	
	Experimental (sterilized ore)	{3130	0,12	25	0	97,3	2,7	Copious black deposit of nontypical Metallogenium
		{3131	0,25	23	0	97,5	2,5	
	Experimental (2/3 s + 1/3 o)	{3134	0,26	39	0	98,3	1,7	Black deposit of nontypical Metallogenium
		{3135	0,21	29	0	97,1	2,9	

(Table continued on following page)

*Commas represent decimal points.

TABLE 4. (Continued)

Lake, Series	Composition of silt (s), addi- tion of ore (o)	Vessel No.	Silt solution			Microgrowths in peloscopes		
			Avg. Eh, V	Avg. Mn ²⁺ mg/l	Avg. Fe ²⁺ mg/l	Mn ₂ O ₃ %	Fe ₂ O ₃ %	Composition of microflora
Punnus XXI	Control	5151 5152	-0.12	23	1.5	66.9	33.1	{ Two-colored deposit of typi- cal Metallogenium and Siderococcus
	Experimental (4 s + 1 o)	5153- 5156	0.11	22	0.1	94.5	5.5	{ Black deposit of typical Metallogenium
Kirkko XXIII	Control	5177- 5180	-0.24	30	4.4	86.0	14.0	{ Black deposit, in part above the silt. A weak ochre- colored deposit of Siderococcus
	Experimental (41 s + 0.5 o)	5183- 5187	0.27	30	0	94.2	5.8	{ Black deposit in the silt of typical Metallogenium
Kirkko XXVII	Control	8226 8227	-0.25	35	9.1	68.1	31.9	{ Dark-brown deposit above silt of nontypical Metallogenium, ochre-colored deposit in the silt of Siderococcus
	Experimental (1 s + 0.12 o)	8228 8229	0.15	18	0.5	89.8	10.2	{ Brown deposit above silt of nontypical Metallogenium; black deposit in the silt of typical Metallogenium
	Experimental (1 s + 0.5 o)	8230 8231	0.43	24	0.5	89.0	11.0	{ Ditto
	Experimental (1 s + 1 o)	8232 8233	0.54	20	0.4	71.3	28.7	{ Sparse brown deposit above silt of nontypical Metallo- genium; weak black deposit in the silt of typical Metallogenium

(Table concluded on following page)

iron-oxidizing *Siderococcus* in the microzone, and, consequently, reduction sometimes to zero of the admixture of Fe_2O_3 in deposits of Metallogenium.

The addition of the powdered lake ore to the silt sample for an increase of its redox potential can be considered, to a certain degree, as the modeling of those changes which take place from a certain moment during the formation of ore fields in the lakes. One should expect that, as iron oxides continue to accumulate in the silt, there will be a gradual increase of the redox potential of sediment. In time, this will lead to the transition from pure iron-accumulation to the formation of iron-manganese ore concentrates, and subsequently to the predominant manganese deposition. This process can be visualized schematically by an example shown in Figure 3. The horizontal straight line (Γ) denotes an arbitrary upper limit of the reducing layer of the silt. The vertical columns directed downward show the amount of divalent manganese (1) and iron (2) in the silt solution of the reducing layer. The extensions of these columns upward, above the horizontal line (Γ) represent corresponding amounts of the Mn and Fe oxides deposited in the silt and of divalent ions in bottom-adjacent water. The latter are shown by dotted lines. The level of the redox potential of the reducing layer which gradually increases with time is shown schematically in the form of a step-wise curve (Eh).

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At some initial (I) low value of the silt Eh, the silt contains divalent ions of both manganese and iron. They freely diffuse into water near the bottom! Under these conditions, Mn^{2+} remains in solution; but iron becomes oxidized in part by both bacteria and oxygen from the air and precipitates into the sediment layer. The appearance of oxidized iron at the bottom increases the redox potential of the upper layer of deposit and of the bottom-adjacent water. Therefore, the oxidation level of iron is lowered from water to the pelogen. At this step (II), a typical biogenic microzone of iron-bacteria develops in the silt. These bacteria oxidize and precipitate all the divalent iron settling down. The concentration of the

latter in the silt solution decreases, whereas the concentration of manganese ions at this level of the redox potential essentially does not change in the silt, and only a part of the ions which pass into water near the bottom becomes deposited, being oxidized by plankton microorganisms.

Enrichment of the silt with iron oxides and, particularly, the appearance of manganese dioxide in the sediment lead to further increase of Eh of the bottom deposit. At this level (III)

the amount of Fe^{2+} ions in the silt solution rapidly diminishes. They undergo full conversion in the microzone of iron-oxidizing bacteria when they diffuse into the oxidizing level. Under these conditions, the concentration of Mn^{2+} ions decreases only a little. As a result of development in the pelogen of manganese-oxidizing bac-

teria (for instance, Metallogenium), all the manganese diffusing up becomes captured and oxidized. In a sense, a biological screen is formed, preventing penetration of divalent manganese into bottom-adjacent water, although physico-chemical conditions of the water allow still a considerably higher concentration of Mn^{2+} . Along with the continued accumulation of iron oxide, gradual concentration of manganese oxides takes place in the pelogen, and we have an even greater increase of the Eh deposit. At its new level (IV), the amount of Mn^{2+} shows hardly any decrease. On the other hand,

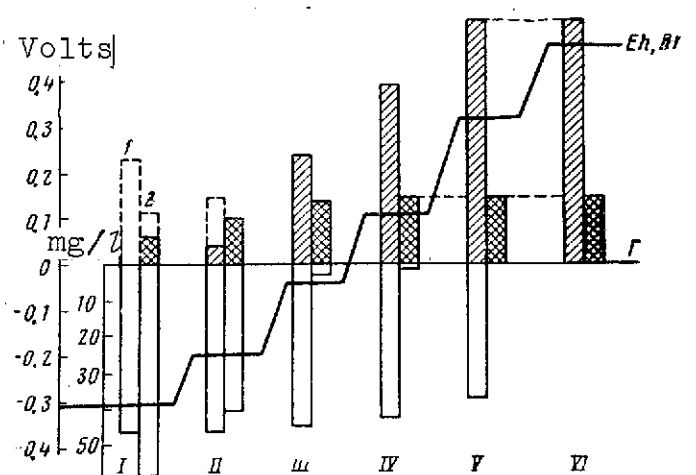


Figure 3. Diagram of the exchange of iron accumulations by predominantly manganese deposits, in connection with the vital activity of the silt microflora in lakes. I - VI — the increase of the redox potential of silt, expressed schematically by the Eh curve. Lower columns — content of Mn^{2+} (1) and Fe^{2+} (2). Upper columns — amount of precipitated oxides of Mn and Fe. Horizontal line r — upper boundary of the reducing layer of silt

divalent iron nearly completely disappears from the silt solution. Consequently, the accumulation of iron oxides in the pelogen is sharply slowed down. Under these conditions, manganese continues to be concentrated intensely by microorganisms in the form of its oxides, and its percent in the bottom deposit sharply increases in comparison with iron oxides; hence the Eh of the deposit further increases. At some still higher value of the Eh level (V), the divalent iron can disappear completely from the silt solution. Therefore, the iron ore formation does not take place now any more, and there is no further accumulation of oxidized iron in the deposit. Manganese will continue to be further oxidized by microbes, and will concentrate, causing even further rise of the deposit Eh. Of course, there will be a certain limiting value of the redox potential of the deposit (VI), after which there will be no further rise of Eh and no further deposition of manganese oxides because of the exhaustion of divalent manganese from the silt solution. We have not observed this in our experiments. Apparently, inhibition of the oxidizing activity of manganese microbes can occur earlier. Indeed, it was observed that the manganese microzone formed more slowly in vessels with the highest additions of ore (Eh above 0.4 - 0.5 volts), and the sediment in peloscopes was sparse and consisted of a nontypical Metallogenium with degraded cenobia.

The fact that such a scheme is not purely hypothetical and can be, to a known approximation, reproduced on laboratory models with secondary silt profiles, follows from a number of experiments considered above, particularly four of them — Series XVIII, XIX, XXIII, and XXVII in Table 4. There is a direct dependence between the amount of added ore (o) to the silt solution (s) — as shown in Column 2 of Table 4 — and the increase of the redox potential of the reducing layer. The reproducibility of these changes is evidenced by numerous graphs characterizing the development of secondary silt profiles (only two graphs were shown for illustration — Figures 1 and 2). In the course of 2 - 3 years, the Eh in control vessels of these series remained definitely negative (from -0.24 to -0.29 volts) and along with Mn^{2+} there was always present a

considerable amount of divalent iron in silt solution. But in samples with addition of relatively small amount of the lake ore (about 0.12 of silt volume) the redox potential markedly increased. During this time, the redox potential in Series XVIII stayed at the level of about 0.11 volts, and in Series XXVII it varied within the limits of 0.16 - 0.20 volts. As could be expected, the amount of Fe^{2+} in these experimental vessels decreased sharply, and then stayed all the time at this new level. In experimental vessels 8230 and 8231, where the Eh was still higher (varying from 0.38 to 0.49 volts), the divalent iron appeared at first and then was practically absent. Whether it disappeared from the silt solution or was reduced to an amount undetectable in samples with a volume of 1.5 - 2 ml in all could be decided only after the analysis of sediments formed in peloscopes of the oxidizing microflora. A similar picture was observed in experimental vessels 8232 and 8233 of the same series, with the highest additions of the ore. The Eh value rose even higher (to an average of 0.54 volts). The divalent iron disappeared. The concentration of divalent manganese was considerable and did not decrease. It was not the residual manganese observed in sterilized silt samples; this manganese appeared in the formation of secondary profiles as a result of the vital activity of the appropriate microflora, since at the beginning of the experiment, the concentration of Mn^{2+} was three times smaller. /585

The scheme of biogeochemical transition from iron ore formation to predominantly manganese ore deposition, considered here, does not, apparently, contradict the existing postulates of the lake ore formation at the present time and in the recent past. As remarked by V. I. Vernadskiy (1954), "the creation of these (i.e., rich in manganese — D. G.) lake iron-manganese ores involves a century-long slow process of the enrichment of iron compounds with manganese; limonites containing manganese become converted in lakes into bog manganese containing iron" (Collected Works, Vol. I, p. 78). In the same book (p. 82), he maintains that "in many cases with certainty, and in others on the basis of a fully justified hypothesis, one can consider the formation of bogs as a result of biochemical processes, for instance, the formation of concretions at the bottom of water basins and in moist areas of the ground surface."

When the silt microflora is eliminated, the formation of the silt profile is considerably disturbed. The character of this change varies, depending on the method of sterilization. For instance, a treatment with formalin eliminates iron (Fe^{2+}) from the silt solution, but the amount of Mn^{2+} increases several times, and these ions appear in large amounts in bottom-adjacent water. Thermal sterilization of the silt solution leads also to the full disappearance of divalent iron from the silt solution; the concentration of Mn^{2+} in the silt solution does not change, but this ion appears in the same amounts in the bottom-adjacent water. The amount of oxygen dissolved in water decreases, and it diffuses into the silt solution where it is utilized slowly because of the absence of microorganisms. Not a single one of the experimental vessels exhibited the oxidation microzone of iron and manganese, so characteristic for the normal silt profile, and the peloscopes lacked the microbial deposits. In short, the process of oxidation and concentration of manganese and iron ceased completely in silts with dead microflora (Gabe, Galperina, 1964).

Both formalin and thermal sterilization lead to certain side changes in the silt, for instance, to intense chemical extraction and reduction of manganese (formalin) or to a strong disturbance of the gaseous regime (autoclaving). In order to prevent these side changes, we utilized an antiseptic — sodium merthiolate — to treat the silt samples. Hopefully, this agent should eliminate the vital activity of all the silt microflora and, at the same time, should not cause any changes in the redox potential in comparison with the control. The concentration of Mn^{2+} in silt solution of experimental vessels did not change. The amount of Fe^{2+} decreased only with time. However, no manganese-iron microzone formed in experimental vessels, and the peloscopes had no trace of microorganisms which oxidize Mn and Fe. Consequently, the nonoccurrence of oxidation and concentration of manganese and iron in silts sterilized with sodium merthiolate, in the presence of divalent ions of both elements in

silt solution and at the normal redox potential level in the silt profile, can be attributed only to the absence of the oxidizing microflora.

In conclusion we should remark that investigation of the ore formation in lakes by the action of microorganisms by means of modeling appears very promising. However, the fruitful development of this methodical approach is possible only when there is concurrent accumulation of data concerning the microorganisms and conditions of their geochemical activity in water basins themselves. Then, the studies should concern the activity of microorganisms in pure cultures on synthetic media. In this connection, studies in recent years are of particular interest on the microbiology of ore formation in some lakes of the Karelia Isthmus (Sokolova-Dubinina, Deryugina, 1967a, b, 1968; Dubinina, 1969; Shterenberg et al., 1969). Only after the consideration of results of similar investigations can we construct models which least distort the natural geobiochemical phenomena. Only then, having data for further experimentation, can we continue to identify the iron-manganese lake ore formation as a bacteriogenic process.

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